PERMEABILITY OF MEMBRANES TO WATER VAPOR WITH SPECIAL REFERENCE TO PACKAGING MATERIALS

By

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ABSTRACT

A study of data from about 30 sources in the literature shows that measurements of the permeability of membranes to water vapor have been made by four types of methods, with many modifications, and that the testing conditions have varied widely. The test period ranged from 2 to 2,000 hours; the temperature from −14 to 45° C; the area of the specimen from 0.15 to 323 cm²; and the vapor-pressure difference from 0 to 72 mm of Hg. Considerable variety was also found in methods of sealing on the specimen, ventilation of the specimen, and units of expressing the results. Data have been reported in at least 20 units.

Sheet materials used in packaging commodities range in permeability to water vapor from that of waxes and rubber to that of textile fabrics. The data indicate that the transpiration of moisture is proportioual to the area, to the time in the steady-state region, and, within certain limits, to the difference in vapor pressure. It is reported by some to be inversely proportional to the thickness also, while others disagree. A seal to prevent edge leakage is of the utmost importance. Temperature requires close control. Relative humidity, especially at high values, and the slowness of diffusion of water vapor through air have a marked influence in many cases.

Suggested mechanisms of moisture transpiration include consideration of gaseous diffusion, diffusion of moisture in solid solution, movement of moisture as a function of the content of hygroscopic moisture, and migration of adsorbed water along surfaces.

CONTENTS

I. INTRODUCTION

Integuments in great variety, including fabrics, leather and animal membranes, rubber and rubberized materials, paint and varnish films, insulating coverings, and wrapping materials, that contribute to the mode of life of modern man, have their usefulness determined in some

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measure by their ability either to permit or to prevent the passage of water vapor through them. It is not surprising, therefore, that considerable attention has been given to means of measuring the rate of passage of water vapor through such materials. An increasingly important class of integuments is the moisture-resistant wrapping and packaging materials that are designed primarily to preserve and protect foodstuffs and other hygroscopic articles of commerce during the period that intervenes between their production and their consumption. The importance of adequate means of testing the permeability of such materials to water vapor is evident, and the interest in such testing methods is widespread. The demand for a standard method of testing wrapping and packaging materials for permeability to water vapor has become so insistent that a subcommittee was appointed some months ago by the Technical Association of the Pulp and Paper Industry (TAPPI) to study the problem.

The reports of a considerable number of investigations that have been made on the water-vapor permeability of various materials during the past 15 years are reviewed in this paper. The information contained in these reports is particularly pertinent in the development of a standard testing method, and is also indicative of many of the difficulties that may be anticipated in working out an adequate standard of measurement, which, at first thought, appears to be a very simple problem.

II. COMPARISON OF TESTING METHODS AND DATA

1. EXPLANATION OF TABLES

Comparative data from the various reports have been assembled in tables 1 and 2. The methods and testing conditions used are listed in table 1, while table 2 gives the results, expressed in a common unit for ready comparison, together with references to the sources of the data. The reference numbers in the tables and in the text correspond to the list of references at the end of the paper.

The testing methods are of four types. The first two methods described below are of the same type, but they are of such significance as to require separate description.

TABLE 1.—*Methods and testing conditions used by various investigators in measuring the permeability of membranes to water vapor*

Reference [1]	Method [2]	Moisture gradient [3]	Over-all vapor-pressure difference	Temperature	Total pressure difference	Area	Test period	Nature of edge seal [4]	Forced circulation [5]	After steady state?	Unit used in report
			mm of Hg	°C	mm of Hg	cm²	hr				
[1]	A	W-A-S-50h		21	0	45.6	16	C only	Rapid	No	g/100 in²/24 hr.
[2]	A	W-A-S-50h	9.3	21	0	32	16	C, rubber gasket	Rapid	Yes	g/m²/24 hr.
[3]	A	W-A-S-warm air	35(?)	37	0	34		"Cemented"	Mod.	Yes	g/hr/m².
[4]	A	W-A-S-A-CaCl₂	50.6	38	0		24	"Sealed tightly"	Mod.	No	g/m²/24 hr.
[7]	A	W-A-S-1h	53	40	0	36	24	Beeswax	Mod.	No	g/100m²/hr.
[9]	C	High h-S-low h	6 to 17	15 to 17	0	16.3	97	C, rubber solution	Slight		g/hr.
[10]	B	W-A-S-A-P₂O₅	23.8	25	0	50.3		Rubber cement	None	No	l/m²/24 hr/atm.
[11]	B	95h-S-A-Al₂O₃	25	27	0	72(?)		"Sealed"	Mod.		hr-cm²/mg.
[12]	A	W-A-S-A-CaCl₂	32	30	0	36	24	"Picein"	None	No	mg/3 hr.
[14]	A	W-A-S-63h	37	38; [6] 21	0	65.5	4	"Seccotine"	None	Yes	g/sec/1,000 cm².
[15]	A	W-A-S-A-CaCl₂	23.8	25	0	213	4	"Sealed"	Mod.	Yes	g/in²/24 hr.
[16]	A	W-A-S-A-0h	23.8	25	0			C, wax, Hg, petrolatum	None		g/cm cube/hr/mm of Hg.
[17]	B	95h-S-A-Al₂O₃	25	27	0	72(?)		Wax	Mod.		mg/hr/cm²
[18]	A	W-A-S-A-H₂SO₄	49.2	38	0			"Sealed"	Mod.	No	mg/m²/hr.
[19]	A	W-A-S-65h	6 to 14	21 to 38	0	25.5	400	Beeswax-rosin	Mod.	Yes	g/hr/m²/mm of Hg.
[20]	A	W-A-S-50h	9.3	21	0	323	168	C, rubber gasket	Rapid	No	g/24 hr/100 in².
[21]	A	W-A-S-A-H₂SO₄	1 to 55	40	0	7.1		Tinfoil, rubber	None	Yes	g/sec/cm².
[22]	A	W-A-S-65h	37	38; [6] 21	0	75		Rubber cement	None	Yes	mg/sec/1,000 cm².
[23]	D	W-V-S-V-P₂O₅	23.8	25	23.8	5	700	C, mercury	None	Yes	mg/hr/cm².
[24]	A	W-A-S-65h	6.1	20	0	200		C, rubber gasket	Rapid	No	g/dm²/hr.
[25]	A	W-A-S-A-H₂SO₄	3 to 32	30	0	7.5	2,000	Shellac, cerate resin	None	Yes	g/in.²/24 hr.
[26]	A	W-A-S-A-0h	6 to 24	21 to 25	0	12.9	900	C, gasket, wax	None	Yes	g/hr/cm/mm of Hg.
[27]	C	100h-S-A-CaCl₂	31.9	30	5	38.7	2	C, petrolatum	Slight	No	g.
[28]	A	W-A-S-50h	9.3	-14, 21	0	42	120	Beeswax	Mod.	Yes	g/m²/24 hr.
[29]	E	100h-S-V-0h	17.5	20	760	0.15	168	C, cork gasket	Slight		g/cm²/sec.
[30]	B	W-A-S-A-H₂SO₄	0 to 72	5 to 45	0	1.27	24	Beeswax-rosin	None	Yes	mg/24 hr.
[31]	B	W-S-A-CaCl₂	55.4	40	0	28	28	"Special wax"	None	No	hr-cm²/mg.
[33]	B	95h-S-A-Al₂O₃	25.4	27	0	72	48		Mod.		hr-cm²/mg.

1 References at end of paper.
2 Methods described in text.
3 W=Water surface; A=air space; V=evacuated space; S=specimen; and h=percentage of relative humidity.
4 C=Clamping ring.
5 Circulation of air in contact with 1 face of specimen: Mod.=moderate; rapid=1 to 3 m/sec.
6 38° on 1 face, 21° on the other.

TABLE 2.—*Permeability to water vapor of various materials reported in the literature* [1]

WATER-VAPOR PERMEABILITY [1] IN g/24 hr/m [2]/mm of Hg

Regenerated cellulose	Moisture-proofed regenerated cellulose	Paper	Waxed paper	Other moisture-proofed papers	Vegetable parchment	Glassine	Waxed glassine	Moisture-proofed fiber board	Asphalt
38 [4]	0.06 [7]	73 [1]	0.04 [27]	0.08 [28]	25 [4]	35 [12]	0.34 [4]	0.2 [2]	1.1 [26]
39 [7]	.1 [4]	74 [2]	.24 [4]	8.0 [28]	70 [20]	48 [1]	7.6 [4]	.2 [28]	---------
67 [1]	.2 [18]	80 [20]	.25 [13]	40 [24]	---------	56 [2]	---------	2.0 [15]	---------
92 [20]	.2 [12]	125 [24]	1.0 [28]	---------	---------	65 [20]	---------	---------	---------
115 [14]	.2 [28]	250 [24]	1.5 [1]	---------	---------	---------	---------	---------	---------
225 [24]	.4 [7]	---------	1.6 [2]	---------	---------	---------	---------	---------	---------
360 [29]	.6 [28]	---------	4.4 [4]	---------	---------	---------	---------	---------	---------
---------	.7 [2]	---------	14 [18]	---------	---------	---------	---------	---------	---------
---------	1.0 [1]	---------	17 [1]	---------	---------	---------	---------	---------	---------
---------	1.6 [24]	---------	18 [2]	---------	---------	---------	---------	---------	---------
---------	---------	---------	120 [27]	---------	---------	---------	---------	---------	---------

Wax	Cellulose acetate	Cellulose nitrate	Cellulose ethers	Protective films[3]	Rubber	Leather	Textile fabrics	Copper gauze	Open cell
0.06 [26]	0.04 [28]	1.4 [31]	10 [26]	0.19 [33]	0.04 [23]	1 [9]	75 [22]	120 [14]	218 [1]
---------	1.1 [26]	6 [31]	20 [20]	.21 [11]	.25 [10]	5 [30]	160 [3]	---------	251 [20]
---------	2 [25]	15 [20]	42 [20]	.3 [17]	.8 [20]	100 [30]	105 [22]	---------	336 [14]
---------	22 [2]	---------	---------	.7 [19]	1.4 [26]	---------	115 [14]	---------	1,327 [1]
---------	44 [1]	---------	---------	5.9 [33]	3.9 [23]	---------	126 [20]	---------	---------
---------	68 [20]	---------	---------	8 [11]	6.5 [26]	---------	130 [14]	---------	---------
---------	150 [26]	---------	---------	15 [17]	9.6 [1]	---------	---------	---------	---------
---------	---------	---------	---------	26 [19]	---------	---------	---------	---------	---------

[1] The numbers in brackets refer to the list of references at the end of the paper.
[2] Values in references [11, 19, 20, and 33] were reported for a thickness of 1 mil (0.025 mm). Values from reference [26] have been calculated to a thickness of 1 mil and likewise all values for rubber.
[3] Includes paints, varnishes, and aircraft finishes.

Method A.—The specimen is fastened over the mouth of a dish or cell (usually a crystallizing dish) containing water, or an aqueous solution of high relative vapor pressure. Loss of moisture through the specimen to a drier atmosphere is determined from successive weighings.

Method B.—As in method *A*, the specimen is fastened over the mouth of a dish or cell, which, however, contains a desiccant. The gain in weight of the cell serves to measure the amount of moisture passing through the specimen and into the cell from a moist atmosphere on the outside.

Method C.—The specimen is a septum between a moist stream of air and a dry stream of air. Moisture that passes through the septum appears as an excess weight in one moisture train or as a deficiency in the other.

Method D.—The specimen is a septum between one chamber containing saturated water vapor only and another chamber that is initially free of moisture, both chambers being evacuated before the water is admitted to the first chamber, in order to allow free diffusion of the water vapor within the apparatus. The permeability is determined either by measuring with a mercury manometer the rate at which the pressure increases in the second chamber or by weighing the transpired moisture absorbed in a desiccant suspended from a calibrated quartz-fiber spring.

Method E.—The specimen is a septum separating saturated water vapor from an evacuated space consisting essentially of a flow tube with an ionization gage at each end. The vacuum pump is kept going all the time and the water-vapor flowmeter measures at any time the rate of flow of moisture through the specimen.

Methods *A* and *B* represent the type of method used in more than three-fourths of the investigations. The significance of the difference between these two methods can be made clearer later on. In some cases more than one method was used, but only the principal method in each case is listed in table 1. Particular mention should be made, however, of one case [19],[1] for which method *A* has been listed in table 1, although method *B*, with 65-percent relative humidity outside the cell, assumed about equal importance in the investigation.

The over-all humidity gradient is listed because in nearly all cases it is not possible to know the vapor pressure at each face of the specimen, since there is an unknown vapor-pressure difference across the air spaces that in most cases separate the moistening and drying agents from the specimen. If the space is free of air it is designated by *V* instead of *A*. The symbol sequence $W-A-S-A-0h$ indicates, for example, that a water surface, *W*, is separated from the specimen, *S*, by an air space, *A*, on one side, and that another air space on the other side intervenes between the specimen and the drying agent that produces presumably a relative vapor pressure, *h*, of zero. The drying agent is listed as such if given in the source. In another column is given the over-all vapor-pressure difference in millimeters of mercury, determined from the temperature and the over-all humidity difference.

In most cases the temperature was the same on the two sides of the specimen. In a few cases tests were made at more than one temperature. In two cases [14 and 22] the temperature was higher on one side of the specimen than on the other. Most tests have been made with atmospheric pressure on each face of the specimen, that is with a total pressure difference of zero. The test periods tabulated are the maximum values reported. Where forced circulation is indicated it refers to the artificial movement of air across one face of the specimen with a fan or other type of impeller. In only one case [9] was forced circulation provided on both faces of the specimen. If the measurements were made after the steady state of moisture transpiration was attained, the fact is indicated by "yes", otherwise by "no." In a few cases the results have been expressed as the reciprocal of permeability, in hour square centimeters per milligram, and referred to as moisture impedance.

In one report [16] the results were given in terms of a centimeter cube, that is, for an area of 1 cm² and a thickness of 1 cm. In another [26], the values were reported on the same basis, but the unit is expressed differently. In either case the dimensional unit is the product of mass and length divided by the product of time, area, and pressure difference, and in the latter case the authors chose to cancel a length (cm) in numerator and denominator, giving the unit g/hr/cm/mm of Hg.

The values in table 2 are in grams per day per square meter of material for a vapor-pressure difference of 1 mm of mercury, having been calculated to this unit as a basis of comparison on the assumption

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[1] Numbers in brackets refer to the list of references to the literature at the end of the paper.

that the amount of moisture passing through the material is proportional to the time, area, and vapor-pressure difference. The conversion thus to a common unit introduces some uncertainty into the values because in some cases the rate of transpiration of moisture does not appear to be proportional to the vapor-pressure difference, and because in most cases the vapor-pressure difference across the specimen alone was not definitely known, since only the over-all vapor-pressure difference was given. The values in the table, therefore, probably tend to be low, especially those for the more permeable materials.

It was not possible to convert all the values to a common thickness, because in many cases the thickness of the material tested was not stated. For some materials the results were originally reported for a thickness of 1 mil, and most of the wrapping materials included in the table were very thin.

In several instances an investigator has reported several values for a given kind of material, in which case only his greatest and least values are shown in the table. Two values from the same source for a given material, therefore, indicate the range of values for this material and investigator.

Waxed papers have been grouped separately because so many values have been reported for this material. Papers moisture-proofed by other means have been put in a different column. Elsewhere in the table moistureproofing includes all methods used, whether by waxing or otherwise.

2. DISCUSSION OF TABLES

Table 1 reveals very little tendency toward standardization of the testing conditions. Pronounced individuality is rather the notable characteristic revealed in the magnitude of the pressure gradient and the means of attaining it, the manner of attaching the specimen, the length of the test period, the range of temperature and pressure difference, the area of the specimen, and the units used to express the results. The test period varied from 2 to 2,000 hours; the temperature from -14 to $45°$ C; the vapor-pressure difference from 0 to 72 mm of mercury; the area from 0.15 to 323 cm^2. Considerable differences were also apparent in the rate of movement of air over the face of the specimen and in the relations of the observations to the steady state of transpiration of moisture. The results have been reported in a score of different units, some of which are unintelligible without a detailed knowledge of the conditions under which the tests were made.

The range of values for water-vapor permeability in table 2 is but a small fraction (much less than a millionth part) of that previously reported for the air permeability of similar materials, for which the range reported was a million millionfold [6]. At one end of the scale, represented by the least-permeable materials in table 2, the water-vapor permeability is 10 to 100 times greater than the air permeability. For a material such as ordinary regenerated cellulose, which is not porous but nevertheless rather permeable to moisture, the water-vapor permeability may be as much as 1,000 times the air permeability. On the contrary, porous materials may be much more permeable to air than to water vapor. The air permeability of some textile fabrics,

representing the other end of the scale, may be as much as a million times their water-vapor permeability. One is somewhat astonished to find the water-vapor permeability of a material like regenerated cellulose, the structure of which is so compact that the air permeability is scarcely measurable, to be about the same as that for fairly open material, such as leather, textile fabrics, and ordinary paper that may be thousands or even millions of times more permeable to air. The values reported for the rate of loss of moisture through copper gauze, or even from an open cell, are no greater (with one exception) than the maximum value reported for the rate of passage of moisture through ordinary regenerated cellulose. Thus is emphasized the conclusion of various investigators that there is no definite relation between the water-vapor permeability and the air permeability, and also the necessity for believing that the mechanism for the passage of moisture through membranes is quite different from that for the passage of air through membranes.

The range of values reported for a given material is in most cases rather large, resulting probably from both the variation in the material and the differences in the methods of testing. A fairly consistent difference in methods of testing is indicated in the tendency for a given investigator to report values higher or lower than those reported by another investigator. For example, references [28, 1, 2, 20, and 24] will usually be found in substantially this order wherever two or more occur in the same column. The best agreement appears in the values for moistureproofed regenerated cellulose, a circumstance that encourages some optimism in regard to rapport among methods, until it is observed that all values reported for this material were obtained by substantially the same method, and that there is nevertheless a twenty-fivefold spread in the values.

Table 2 shows that the permeability of packaging materials to water vapor covers practically the whole range indicated for all the various other materials in the table, which suggests that the experience and information obtained in the other fields should be very helpful in the problem of adequately measuring the permeability of packaging materials. This great range in the permeability of packaging materials to water vapor helps to explain why some of the conclusions and generalizations that have been drawn from experiments with certain types of such materials, particularly with reference to the effect of some of the variables, do not hold when applied to other types of packaging materials.

III. VARIABLES IN THE MEASUREMENT OF WATER-VAPOR PERMEABILITY

The chief variables that have been recognized in studies of the permeability of sheet materials to water vapor are:

1. Time.
2. Area of the specimen.
3. Leakage at the edges.
4. Thickness of the specimen.
5. Vapor-pressure difference across the specimen.
6. Relative vapor pressure at each face of the specimen.
7. Total pressure difference across the specimen.

8. Temperature.
9. Diffusion through intervening air spaces.
10. Von Schroeder effect.

The passage of moisture through membranes is usually considered to be some kind of diffusion process, and is frequently assumed to obey the simple diffusion relation

$$W = KtAp/s, \tag{1}$$

in which W is the amount (mass) of moisture that passes in time, t, through a membrane of area, A, and thickness, s, when the difference in partial pressure of water vapor on the two faces of the membrane is p, the coefficient of diffusion being denoted by K. Most of the variables listed above can be thought of as contained, either explicitly or implicitly, in such an expression that attempts to define the relation of the variables. A study of the literature, however, reveals considerable limitation on the operation of so simple a relation as the above equation.

1. TIME

A necessary condition in testing water-vapor permeability is of course a difference in humidity on the two faces of the specimen. In hygroscopic or sorbing materials, the normal uniform distribution of moisture must therefore give place to a gradation from a high value on one face to a low value on the other, in keeping with the two humidity conditions that produce the vapor-pressure difference. This process requires time, and in some cases considerable time. Eventually, if the humidity conditions are kept constant, a steady state is attained such that at any point within the membrane the moisture content no longer changes with time, and such that the rate at which moisture is passing through the membrane becomes constant. During the initial or unsteady state the moisture interchange may be either greater or less than that in the steady state, depending upon the initial moisture content. The duration of the initial period of adjustment and change in rate of transpiration will vary with the nature of the material. It may be a few minutes, or it may be several days. A day or two is ordinarily considered sufficient to bring about the steady state in packaging materials, although data are on record of materials that required several weeks for the steady state to be attained [7, 26]. Occasionally a surface resistance or skin effect has been postulated to explain apparently anomalous results that may have resided simply in the normal lag in the adjustment of the concentration gradient and the failure of the observer to wait long enough before taking the first reading.

Provided the initial period of uncertain rate is excluded, the transpiration of moisture has been reported in nearly all cases as being proportional to the time, in accordance with equation 1. It is a somewhat curious fact, however, that, although nearly all workers have calculated and reported their results on the assumption that the amount of moisture passing through the membrane is proportional to the time, only about half, according to table 1, seem to have waited until after the steady state was attained before beginning to reckon the time used in the calculation.

2. AREA OF THE SPECIMEN

Although table 1 shows that the largest area used is more than 2,000 times as great as the smallest, the obvious assumption of direct proportionality between the rate at which moisture passes through a membrane and the amount of surface exposed has been questioned in only one report [2]. In this case the anomalous behavior was attributed to the shape and proportions of the test cell, although it may possibly have arisen from uncertainty as to the actual area involved, an uncertainty arising from the manner of attaching the specimen to the cell.

There seems to be, in fact, room for more or less uncertainty about what the actual exposed area is in many cases. Although exact delineation of area is a virtue attributed to special forms of cells designed to seal by means of clamping rings rather than by the inelegant smearing of wax, such devices (with the possible exception of one that makes use of a soft, waxed gasket) probably do not define the area definitely, because of the probability of (a) edge leakage and (b) diffusion of moisture within the unsealed space between the clamping surfaces. It is evident that the manner of securing or sealing the edges of the specimen must be reflected in the effective area. Edge leakage, or diffusion of moisture into the clamped area, must operate to increase the effective area, while methods of sealing a membrane to a crystallizing dish (the form of cell used in half the studies listed in table 1) usually result in an area with irregular boundary that is not sharply outlined and that makes difficult the measurement of the area. Efforts have been made to decrease the uncertainty and variation in the effective area. The method recommended in 1934 by the TAPPI container committee [8], and since used in modified form by others [7, 28], is said to yield a free area that is fairly reproducible, although it is somewhat smaller than that of the mouth of the dish. A recent method devised by Kline [19], in which the specimen is sealed with a mixture of beeswax and rosin between two aluminum rings, one of which is fastened permanently to a crystallizing dish, yields a fairly definite area. Molding the edges in wax, with the use of a templet to define the area, has also given good results.

3. LEAKAGE AT THE EDGES

The reliability of tests of relatively impermeable materials depends largely on the effectiveness of the edge seal, without which the leakage may easily amount to more than the moisture passing through the membrane. Edge leakage has been attributed to two sources: (a) leakage between the face of the specimen and the rim of the cell, and (b) leakage laterally through the material itself with gain or loss of moisture through the cut edges. If the latter form of leakage is significant, table 1 suggests a false sense of security in a few cases where reliance has been placed on mechanical clamps and gaskets. Most investigators who have reported on relatively impermeable materials have sealed the specimen to the cell with such materials as beeswax, beeswax and rosin mixture, rubber solution, petrolatum, shellac, and various other sealing waxes. Some make clear that the cut edges have been sealed, while others are obscure on this point. Immersion of the edges in mercury in a suitably designed cell is another

method used in sealing the edges. According to table 1, the workers most remiss about sealing the edges are found among those who have reported chiefly on packaging materials. It is probably significant that there is a fairly consistent correlation between the magnitude of the values for moistureproofed regenerated cellulose in table 2 and the uncertainty in the effectiveness of the edge seal provided by the different workers.

4. THICKNESS OF THE SPECIMEN

Although equation 1 may hold for simple gaseous diffusion, less certainty attends the assumption that the rate of transpiration is inversely proportional to the thickness when the process is modified by sorption, as when water vapor is passing through certain membranes. Evidence that such a relation does not hold is found [23], although others have concluded that the relation may or may not hold, depending upon the type of testing method used, the nature of the material, and the effect of sorption at high humidities [26]. Other workers report that the moisture impedance (reciprocal of the permeability) is substantially proportional to the thickness or linearly related to it [31, 33]. Many have calculated their reported results on the basis of the relation in equation 1.

Most of those who have tested the permeability of packaging materials to water vapor have made no attempt to calculate their data to a unit thickness, realizing perhaps that such materials are not subdivided in thickness after fabrication, that in some cases the thickness provides part of the resistance to transpiration while in others this resistance resides almost wholly in a relatively thin surface film, and that the overall permeability of a packaging material is of more importance than its unit-thickness value, particularly in relation to a consumer standard.

5. VAPOR-PRESSURE DIFFERENCE ACROSS THE SPECIMEN

The vapor-pressure difference seems less amenable to the simplicity of equation 1 than the other quantities therein. Although a number of workers have found that under certain conditions the rate of passage of moisture through a membrane is proportional to the difference in partial pressure of the water vapor across it [1, 7, 11, 21, 24, 25, 26], most of them have found also that for other conditions the rate of moisture transpiration is not proportional to the difference in vapor pressure. Frequently the vapor-pressure difference across the membrane alone cannot be determined from the conditions of the test, which is another serious difficulty in determining quantitatively the effect of the vapor-pressure difference on the permeability.

Although it is difficult to weave the various findings into a consistent pattern, there is fairly good agreement among different workers on the following relations:

The rate of transpiration of moisture is proportional to the difference in vapor pressure for all ordinary conditions (a) for those materials that do not take up appreciable moisture from the atmosphere, whether the change in vapor-pressure difference is produced by change of temperature or of relative humidity; (b) for hygroscopic or sorbing materials, provided the relative humidity at each face of the sheet remains constant throughout; and (c) for sorbing materials when the

relative humidity does not remain constant when the vapor-pressure difference is varied, provided the relative humidity and the moisture-content gradient do not rise above certain limits that are different for different materials.

The rate of transpiration of moisture is not proportional to the difference in vapor pressure (a) for sorbing materials of low permeability when the change in vapor-pressure difference is produced by altering the relative humidity, if this relative humidity exceeds 70 or 80 percent on one face of the sheet; and (b) for sorbing materials of high permeability at practically all values of the relative humidity when the change in vapor-pressure difference is being produced by changing the relative humidity (for instance, by changing the vapor pressure at constant temperature).

6. RELATIVE VAPOR PRESSURE AT EACH FACE OF THE SPECIMEN

That the relative vapor pressure, as well as the difference in vapor pressure, is an important factor in water-vapor permeability is suggested by the above relations. Because of the well known dependence of moisture content on relative humidity, it is not a surprise to find in several reports [11, 24, 25, 26, 33] the suggestion that the rate of passage of moisture through a membrane is probably closely connected with the amount of moisture normally taken up by the membrane from atmosphere of given relative humidity. For leather, however, its moisture content has been reported to be without influence on the water-vapor permeability [9]. On the other hand, one investigator [24] believes that the water-vapor permeability of cellulosic materials depends primarily upon the moisture-content gradient in the membrane, determined by the relative humidity at the opposite faces.

7. TOTAL PRESSURE DIFFERENCE ACROSS THE SPECIMEN

The effect of a difference in atmospheric pressure, or total pressure, on the two faces of the specimen, which manifests itself in bulging or stretching an unsupported specimen, may be to increase the apparent moisture permeability by breaking the edge seal, by inducing air flow or leakage at the edges, or possibility by opening up the structure of the membrane or decreasing its thickness as a result of stretching it. To such effects must probably be ascribed an observed increase in the apparent water-vapor permeability of cellulose acetate sheeting as a result of putting a partial vacuum on one face of the specimen while keeping constant the aqueous vapor-pressure difference [1]. The moisture permeability of a porous sheet would probably be augmented by a difference in total pressure, by reason of the moisture carried through with the induced air flow, but cellulose acetate sheeting is practically impervious to air. Another effect that might be suspected in such a case is the increased rate of diffusion of water vapor through still air, separating the conditioning agent from the specimen, that would result from decreasing the total pressure therein. In the above case, however, the partial vaccuum was applied only on the external face of the specimen that was normally in contact with air kept in motion by means of a fan.

Another total pressure effect in methods *A* and *B* is associated with changes in barometric pressure between weighings, when there is a relatively large volume of air confined in the cell. A tare having a fixed volume of confined air equal to that in the cell has been used by some to compensate for the difference in density of air inside and outside the cell, resulting from change in barometric pressure between weighings. Overcompensation is likely in such a case, however, since the membrane is somewhat distensible. The better remedy seems to be to reduce the volume of air confined in the cell to such an extent that the distensibility of the membrane is sufficient to prevent a significant difference in density from arising under any ordinary circumstances.

8. TEMPERATURE

Since the vapor pressure depends on the temperature, equation 1 suggests that a temperature change would be felt only to the extent that it alters the vapor-pressure difference across the specimen, provided of course that the membrane itself is not significantly altered by the change in temperature. A number of investigators [1, 7, 11, 21, 24, 25] report that the rate of transpiration of moisture is governed by the vapor pressure difference irrespective of the temperature (except for high temperatures or humidities). A particularly interesting experiment has been recorded [11] in which the vapor-pressure difference was kept constant, while the temperature and relative vapor pressure were varied over a considerable range. The rate of transpiration of moisture remained practically constant, irrespective of temperature, until the relative humidity on one face exceeded about 70 percent, when the rate of transpiration began to increase (even though the temperature was decreasing). Others [19, 26] have reported, however, an increase in water-vapor permeability (per unit pressure difference) with increasing temperature, when a constant relative vapor pressure was maintained on each face.

Temperatures somewhat above the summer range have been reported to be very damaging to packaging materials [7], the increased permeability to moisture having been ascribed to softening of the wax or moistureproofing substance. However, increased edge leakage under the conditions at the higher temperatures might conceivably be partially responsible for the large increase observed in the apparent permeability to moisture. Damage by condensation of moisture on the surface has also been reported. Such condensation may occur during a test by a slight lowering of the temperature when saturated or nearly saturated water vapor is in contact with one face of the specimen.

9. DIFFUSION THROUGH INTERVENING AIR SPACES

The diffusion of water vapor through still air is relatively slow, an influence that has in large measure been ignored. In most tests of water-vapor permeability that have been made, at least one face of the membrane has been in contact with a layer of still air separating it from the humidifying or the desiccating agent. If the rate of flow of moisture through the membrane is great enough to prevent a substantially uniform distribution of moisture within the air space, the

usual assumption that the vapor-pressure difference across the membrane is given by the known over-all vapor-pressure difference is subject to considerable uncertainty. The few data that have been reported with respect to this influence indicate that the vapor-pressure gradient across such an air space may be surprisingly large when very permeable materials are tested. According to one report on tests of cellulose acetate sheeting, glassine, and filter paper, from one-third to more than nine-tenths of the vapor-pressure drop took place through the layer of air confined in the cell under the specimen [2]. Under such circumstances it is evident that the actual vapor-pressure difference across the specimen itself may be but a small fraction of that ordinarily assumed when the pressure drop through the air space is ignored. In another report of tests of materials very permeable to water vapor, including regenerated cellulose sheeting and textile fabrics, the vapor-pressure drop through a half-inch layer of confined air was so great in comparison with that through the specimen alone that substantially the same value was obtained for each of the different materials tested [14]. It is probably significant that there is a fairly consistent inverse relationship between the values (obtained by method *A*) in table 2 for paper and ordinary regenerated cellulose and the distance in each case between the specimen and the surface of the water in the cell.

Although no simple means seems to have been found to minimize the effect of air confined within the test cell, except by making the air space as thin as posssible,[2] the conditions in most cases have been such as to allow forced circulation of the air in contact with the other face. In fully a third of the cases, however, no effort was made to circulate the air over the exposed face of the specimen, and in very few cases has rapid circulation been provided (table 1). There is, of course, considerable difference of opinion as to the amount of circulation that is required, doubtless because of the differences in permeability of the materials in question. The more permeable the material, the more difficult it becomes to prevent vapor-pressure gradients in the air spaces. One report indicates that the water-vapor permeability when no circulation is provided may be only a third as much as when rapid circulation is provided [7]; another concludes that rapid circulation increases the permeability a few percent over very slow circulation [1]; while still others conclude that a slight circulation is sufficient [9, 32].

Although the effect of diffusion through intervening air spaces may be small when relatively impermeable materials are tested, it seems logical, especially in the case of the more permeable materials, where the effect may be large, to minimize this effect by reducing as much as possible the thickness of the layer of air confined in the test cell, and to provide sufficient circulation on the exposed face of the membrane to prevent an appreciable vapor-pressure gradient from existing outside the membrane. Otherwise it is very difficult to know much about the vapor-pressure difference across the membrane itself. The reduction in the thickness of the air space under the membrane is more conveniently made in method *B* than in method *A*, which

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[2] In a modification of a method devised by John, which was described by Drewsen at a recent symposium on water-vapor permeability conducted by TAPPI (unpublished), the cell is filled with a desiccant in granular or lump form and is rotated in a vertical plane so that the tumbling of the particles of the desiccant against the specimen keeps the air well stirred. This method seems to have merit if it can be shown that no harm arises from having the desiccant in contact with the specimen.

seems to be an important point in favor of the use of a solid desiccant in the cell rather than water or other liquid agent.

Results that have been reported for papers differing only in the time of beating the pulp are somewhat enigmatical and may involve the effect of diffusion through still air. Very porous papers (made from lightly beaten pulp), although found to be very permeable to air, were reported as but slightly more permeable to water vapor than the very dense sheets (made from heavily beaten pulp) that were almost impermeable to air [24]. A somewhat similar behavior is shown in table 2, in that nonporous regenerated cellulose sheeting and ordinary porous papers have substantially the same water-vapor permeability, although the air permeability of the latter would be found many thousands of times greater than that of the former. It is not unlikely that the explanation of such behavior may have to take account of the slow diffusion of water vapor through the air confined in the pores of the paper under the usual conditions provided for testing water-vapor permeability. There is good reason for believing that the pores of paper are very long and sinuous [6], and that the resistance to diffusion of water vapor through the air in these pores may well be comparable to the resistance of the cellulose itself to the passage of moisture. Tests in the absence of air of the permeability of paper to water vapor would likely give much higher values than the usual tests in air with a total pressure of 1 atmosphere on each face of the specimen.

10. VON SCHROEDER EFFECT

Some colloidal materials absorb more water when in contact with the liquid than when in contact with saturated water vapor. This Von Schroeder effect, so named from the man who first noted it, is so familiar to the paper technologist that he is likely to think of it as the universal behavior of membranes. Since an increase in moisture transpiration is usually associated with an increase in moisture absorption, we may expect the Von Schroeder effect to have a bearing on the permeability of membranes to water vapor. The testing of materials that do not exhibit the Von Schroeder effect may be simplified by allowing the moisture to enter the membrane from water in direct contact with the membrane [19, 31]. Behavior that might be termed a negative Von Schroeder effect has been reported by one investigator [11]. Since paper and other cellulosic materials usually show the Von Schroeder effect, and since deterioration of certain packaging materials resulting from contact with water has been reported, it seems preferable in the testing of wrapping and packaging materials to avoid the use, not only of liquid water, but also of saturated water vapor on either face of the specimen.

IV. MECHANISM OF THE PASSAGE OF MOISTURE THROUGH MEMBRANES

In the main the passage of moisture through membranes has been explained as being due to (a) gaseous diffusion; (b) diffusion of water in solid solution; (c) movement of moisture along a concentration gradient determined by the difference in moisture content at the two faces of the membrane, or (d) adsorption of water vapor and the migration of the adsorbed particles along internal surfaces.

Gaseous diffusion may be the means whereby small amounts of water pass through nonpolar substances that have little sorbing tendency toward water vapor, but the passage is perhaps better described by saying that the membrane acts as a molecular sieve [26], since the water molecules are probably always within the sphere of influence of the molecules of the solid during transit. However, gaseous diffusion as a factor in the passage of moisture through sorbing materials, especially nonporous membranes such as the majority in table 2, can probably be dismissed as insignificant. It has already been pointed out that water-vapor permeability bears no definite relation to air permeability. Rubber has been reported as about 50 times as permeable to water vapor as to hydrogen [10]. Various gas-cell fabrics used in airships, although nearly impermeable to hydrogen or helium, permit troublesome amounts of water to pass from the atmosphere into the interior of the gas cells. Ordinary regenerated cellulose, although practically impermeable to air, allows moisture to pass through readily.

The passage of water vapor, as well as of gases in general, through a membrane is frequently thought of as occurring by solution of the gas or vapor on the high-pressure side of the membrane, diffusion in solid solution through the membrane, and evaporation from the surface on the low-pressure side [10, 13, 33]. This view conforms with the generalization that like substances dissolve like substances, and with the observation that membranes are permeable to gases and vapors somewhat in proportion to the "solubility" of the gases or vapors in the membranes. On the other hand, several objections have been made to the solid-solution hypothesis. There is some doubt about diffusion in solid solution being fast enough to account for the relatively high permeability to moisture of such materials as regenerated cellulose and some of the cellulose esters and ethers. Also, diffusion of this sort seems to imply a uniform concentration gradient through the membrane, whereas there is good evidence that the concentration gradient is not uniform [21, 26]. The most important objection advanced, however, is that solid solution of water, in cellulose at least, is incompatible with X-ray evidence, in that water does not enter the crystallites, shown by the fact that the dimensions of the crystal lattice remain unchanged when the water is taken into the structure [5].

Numerous allusions have been made in the literature to a relation between the water-vapor permeability and the moisture content of substances. The explanation of permeability involving this relation grows out of familiarity with the fact that most colloidal materials have a characteristic equilibrium moisture content for a given relative humidity and temperature. It is assumed, quite obviously, that if a membrane separates two bodies of water vapor of different degrees of saturation the moisture content of a thin skin at each face approaches the equilibrium value for the relative vapor pressure on that face. Within the membrane the moisture content declines gradually from the more humid to the drier side and a flow of moisture through the membrane follows at a rate that is assumed to be proportional to the moisture content gradient. In support of this view it is claimed that the relative permeability of papers made alike except for the fiber composition may be predicted from the equilibrium moisture content

of the pulps [24]. The weakness of such an explanation, however, is that it does not elucidate the mechanism of water-vapor transpiration, and seems little more than a restatement of the observed fact that moisture does tend to pass through a membrane when the two faces are exposed to different humidities. That the permeability is not determined by the moisture-content gradient alone follows from experiments such as that mentioned in a previous section concerning the effect of change in temperature. There reference was made to an experiment so devised that the moisture-content gradient varied over a considerable range (by change of temperature and relative humidity), while the pressure difference remained constant [11]. Under these conditions the water-vapor permeability remained constant also, except at high humidity, bearing no definite relation to the moisture-content gradient.

That adsorption phenomena have an important bearing on the mechanism of water-vapor permeability has been suggested by some workers. It is, in fact, impossible to ignore the role of adsorption in water-vapor permeability in view of its widespread acceptance in the explanation of the sigmoid curve of moisture content, or regain, obtained in the case of so many colloidal materials. To make use of adsorption in explaining the mechanism of the transpiration of moisture is but a corollary to its use in the explanation of moisture-content relations, since migration of the moisture within the material is as necessary in one case as in the other. The enormous surface required in the explanation of moisture-content relations in terms of adsorbed water, affording also the locale for the migration of the moisture through the material, is provided in the micellar hypothesis about which much has been heard in recent years in connection particularly with the structure of cellulosic materials. The surfaces of separation between the crystallites or micelles are presumed to be regions where adsorption can take place, from which it may also be inferred that the regions between the crystallites serve as the paths for the migration of adsorbed water through the material.

Some of the implications of adsorption phenomena in relation to the passage of moisture through membranes have recently been indicated in a stimulating discussion [26] in which it is pointed out that particles ionized by adsorption have peculiar properties favorable to their penetration into colloidal materials; that spreading forces characteristic of the adsorbed particles favor the process of transpiration; and that the energy associated with adsorption and desorption probably exerts an important influence. Moreover, it is pointed out that a structure may be impermeable to molecules that are not readily adsorbed, and yet adsorbed water molecules may be able to penetrate it, probably by the sharing of electrons with atoms on the surfaces, and by migration along internal surfaces.

Swelling and evolution of heat (heat of adsorption) are additional manifestations in keeping with the view that adsorption phenomena are responsible for the spontaneous passage of moisture through a membrane when a difference in humidity exists at the two faces. Presumably at the more humid face the adsorbed molecules are several layers deep, and the number of layers diminishes as the drier face is approached. Since the force with which a molecule of water is held to the surface is greater the nearer the molecule is to the adsorbing surface, the force of adsorption in the steady state must therefore

increase continuously from the more humid to the drier side, favoring continuous migration toward the latter.

The striking similarity between the sorption isotherm and that of water-vapor permeability has been remarked in several reports, the slope of the curves in each case having been observed to increase rapidly above a relative humidity of 70 or 80 percent [7, 11, 26]. In one of these reports [11] it is strongly hinted that the permeability behavior may have the same explanation as that for the moisture-content behavior in which it is assumed that, in the region where the slope of the curve is constant, adsorption occurs on the micellar surfaces, and above this region water in a more mobile state condenses in the intermicellar spaces and is accompanied by considerable swelling. The idea of a surface region of strongly adsorbed water molecules enveloping an inner region of relatively mobile molecules having properties comparable to those of a liquid has frequently been advanced with minor variations in explanation of the sorption isotherm. The idea is no less useful in explaining the effects observed in the passage of moisture through membranes.

In this view of the mechanism, although the rate of transpiration is presumed to be proportional to the difference in vapor pressure at the two faces (except at high humidity), as in the case of simple diffusion, the process differs from diffusion in the important particular that migration cannot be random in three dimensions, but must take place by migration of adsorbed particles along surfaces, or definite paths. If the conditions are such that, in addition to adsorption on the micellar surfaces, the intermicellar spaces grow and become filled (perhaps by capillary adsorption in accordance with the theories of Zsigmondy and others) with water not bound to the surfaces, there is superimposed upon the migration along the micellar surfaces a movement, more like ordinary diffusion, of this more mobile variety of adsorbed moisture. This condition would ordinarily exist only near the face of the membrane exposed to a high humidity, and would therefore involve only a part of the thickness of the membrane. The effect, however, would be to accelerate rapidly the rate of transpiration of moisture in the manner commonly observed when one face of the membrane is exposed to saturated water vapor, or a very high relative humidity.

V. IMPLICATIONS WITH RESPECT TO A STANDARD TESTING METHOD

The information derived from the literature that is most useful in arriving at uniform practice and procedure in testing the permeability of packaging materials to water vapor may be summarized in the following statements.

The simplest and most popular type of testing method employs a dish or cell, the mouth of which is closed with the membrane to be tested. A constant vapor-pressure difference is maintained across the membrane, and the change of the weight of the cell with time measures the rate at which moisture passes through the membrane. Although special forms of cells have been described [2, 20, 24, 26], most workers have been content to use crystallizing dishes or other common laboratory equipment.

Another technique that deserves consideration is the use of a desiccant in a basket attached to a quartz-fiber spring balance to measure the moisture transpiration. Its special merit is a continuous indication of the transpiration without interruption of the constancy of the testing conditions.

It is of the utmost importance to seal the specimen to the cell in such a manner as to prevent edge leakage. A wax has usually been employed to make an effective seal.

Water vapor of suitable degree of saturation, rather than liquid water, should be in contact with one face of the specimen.

The total pressure difference should preferably be zero for tests in air.

For of a consumer standard, no account need be taken of the relation between the permeability of packaging materials and their thickness.

The thickness of the layer of air enclosed within the cell should be as small as possible, and the air in contact with the exposed face of the membrane should be stirred sufficiently to prevent an appreciable external vapor-pressure gradient.

A fairly large area is desirable, because it affords better sampling, and because it increases the amount of moisture passing through in a given time, in a test that is ordinarily very time-consuming. Although the effective area of the specimen is frequently indefinite, it can be made fairly definite by certain devices described in the literature [7, 8, 19, 26], or by suitably molding the edges in wax, making use of a templet to limit the exposed area. If the area is definitely known, the transpiration may be calculated to that for a unit area by simple proportion.

The transpiration may in like manner be calculated to that for a unit time, provided the data used have been obtained after the steady state of transpiration has been attained.

If one face of the membrane is in contact with a very high relative humidity, the rate of transpiration is not, in general, proportional to the vapor-pressure difference. If however neither face is subjected to a relative humidity greater than about 70 or 80 percent, it is permissible, with few exceptions, to calculate by simple proportion the rate of transpiration for unit vapor-pressure difference, provided of course the vapor-pressure difference across the membrane alone is known.

Close control of temperature is required because of the large effect of temperature change on the vapor pressure. Within certain limits, however, it is permissible to calculate data from any ordinary temperature to a standard temperature by taking account of the effect of temperature on the vapor-pressure difference.
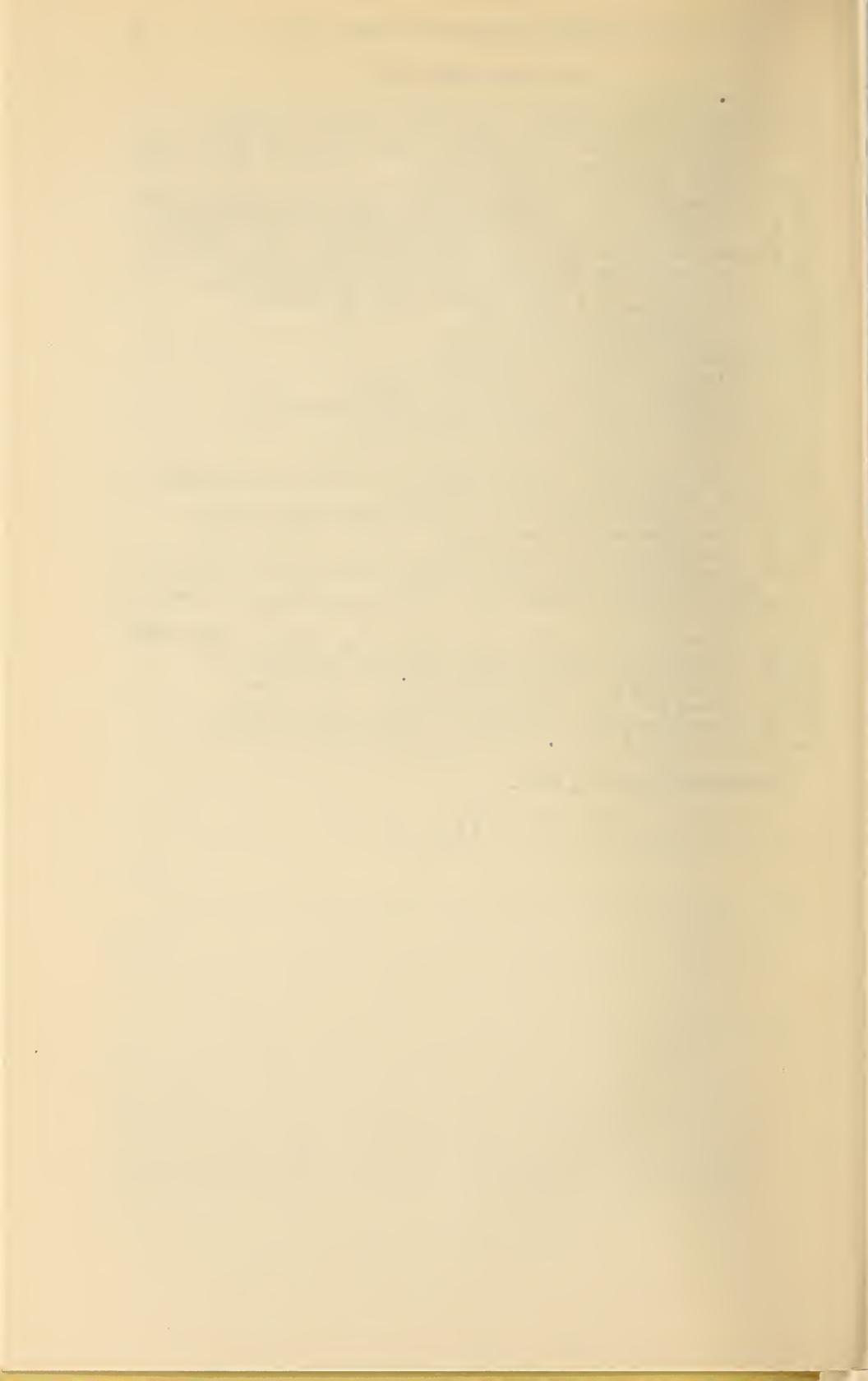
For a standard method, the use of a dry (solid) desiccant in the cell and 65-percent relative humidity on the external face of the membrane would have the distinct advantages (a) that the desiccant can be brought very close to the membrane so as practically to eliminate the enclosed air space; and (b) that 65-percent relative humidity is already standard and widely available in the testing of paper and textiles, and is not much below the maximum value that could be used without getting into the region where the rate of transpiration of moisture is not proportional to the vapor-pressure differences.

VI. REFERENCES

[1] A. Abrams and W. A. Chilson, Paper Trade J. **91**, TS193 (1930).
[2] A. Abrams and G. J. Brabender, Paper Trade J. **102**,, TS204 (1936).
[3] G. Barr, Fabrics Coordinating Research Committee, Dept. Sci. Ind. Research, Gr. Brit., Second Report, p. 132 (1930).
[4] C. Birdseye, Ind. Eng. Chem. **21**, 573 (1929).
[5] W. B. Campbell, Dept. Int., Canada, Forest Service Bul. 84, p. 19 (1933).
[6] F. T. Carson, BS J. Research **12**, 567 and 587 (1934), RP681 and RP682.
[7] W. H. Charch and A. G. Scroggie, Paper Trade J. **101**, TS201 (1935).
[8] Container Committee, Tech. Assn. Pap. (TAPPI), series 17, no. 1, 40 (1934).
[9] R. S. Edwards, J. Int. Soc. Leather Trade Chem. **16**, 439 (1932).
[10] J. D. Edwards and S. F. Pickering, BS Sci. Pap. **16**, 327 (1920) S387.
[11] J. D. Edwards and R. I. Wray, Ind. Eng. Chem. **28**, 549 (1936).
[12] K. Fabel, Kunstseide **15**, 383 (1933).
[13] T. Graham, Phil. Mag. [4] **32**, 401 (1866).
[14] J. Gregory, J. Text. Inst. **21**, T66 (1930).
[15] A. R. Harvey, Paper Trade J. **78**, TS256 (1924).
[16] D. B. Herrmann, Bell Lab. Record **13**, 45 (1934).
[17] J. K. Hunt and W. D. Lansing, Ind. Eng. Chem. **27**, 26 (1935).
[18] W. L. Hyden, Ind. Eng. Chem. **21**, 405 (1929).
[19] G. M. Kline, J. Research NBS **18**, 235 (1937) RP974.
[20] H. A. Levey, Plastic Prod. **11**, 52 (1934).
[21] J. F. Martley, Forest Products Research, Dept. Sci. Ind. Research, Gr. Brit., Tech. Pap. 2 (publications 1926–30).
[22] P. D. Sale and A. F. Hedrick, BS Tech. Pap. **18**, 540 (1924), T266.
[23] E. E. Schumacher and L. Ferguson, Ind. Eng. Chem. **21**, 158 (1929).
[24] W. Staedel, Papier-Fabr. **31**, 535 (1933).
[25] S. T. C. Stillwell, Forest Products Research, Dept. Sci. Ind. Research, Gr. Brit., Tech. Pap. 1 (publications 1926–30).
[26] R. L. Taylor, D. B. Herrmann, and A. R. Kemp, Ind. Eng. Chem. **28**, 1255 (1936).
[27] C. A. Thomas, and H. J. Reboulet, Ind. Eng. Chem., Anal. Ed. **2**, 390 (1930).
[28] D. K. Tressler and C. F. Evers, Paper Trade J. **101**, TS113 (1935).
[29] J. J. Trillat and M. Matricon, J. Chim. Phys. **32**, 101 (1935).
[30] J. R. Wilson and G. O. Lines, Ind. Eng. Chem. **17**, 570 (1925).
[31] H. J. Wing, Ind. Eng. Chem. **28**, 786 (1936).
[32] S. Wosnessensky and L. M. Dubnikow, Kolloid-Z. **74**, 183 (1936).
[33] R. I. Wray and A. R. Van Vorst, Ind. Eng. Chem. **25**, 842 (1933).

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